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MASS SPECTROMETRIC STUDIES OF LASER-PRODUCED
VAPOR SPECIES

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ABSTRACT

The results of mass spectrometric studies of laser-induced vaporization of numerous semi-metallic substances are presented and compared with mass spectra of these substances obtained by other methods of vaporization. Significant differences in the type, relative abundance, size and the number of species present have been observed. The conditions of the laser-induced vaporization are discussed, and it is shown that in this case vaporization takes place under the conditions of high temperatures and pressures, close to the critical values for the substances studied.

INTRODUCTION

Mass spectrometric techniques have been used to study laser-produced vapor of many materials: carbon^{1,2}; several organic compounds^{3,4}; various metals and oxides⁵⁻⁷ and the rare gases⁸. In our laboratory various organic compounds⁹⁻¹¹, elements of groups V-A and VI-A¹²⁻¹⁵ and the V-A-VI-A compounds^{13,14,16,17} have been studied.

In this paper we shall summarize our results given in other papers as well as introduce some new data in order to draw general conclusions about the interaction lasers with semi-metallic substances. Also, where data are available, we shall contrast the laser-produced vapor with the vapor resulting from "conventional" heating of the same substance.

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CONDITIONS OF THE LASER-INDUCED VAPORIZATION

In our experiments a laser capable of producing focused energy fluxes of about 10^7 W/cm² was used. When a laser beam of such power interacts with solids a very fast temperature-rise occurs, and the boiling point is attained in about 10^{-7} sec¹⁸. A thin vaporizing layer moves into the solid at a steady state rate (10^2 – 10^3 cm sec⁻¹), and a crater is formed^{19,20}. The resulting vapor escapes in the form of a rapidly expanding jet, moving with a speed of 10^4 – 10^5 cm sec⁻¹ (refs. 19, 21). The recoil pressure exerted on the condensed phase by this rapidly expanding vapor is estimated to be over 1000 atmospheres in the case of 1-5 J lasers operating in the normal pulsed modes^{22,23}. Pressures of this order are sufficient to keep many materials in their condensed state up to temperatures far above their normal boiling points (T_b). In some cases superheating to critical temperatures is possible. Although the critical temperatures for most of the substances we studied are not known we can estimate them to be $2.5 T_b$ or less^{24,25}. Since we are dealing with substances generally having $T_b < 1500^\circ\text{K}$ the critical temperatures will be 3500°K or lower. Experimental^{26,27} as well as theoretical¹⁹ temperature determinations show that in the laser-solid interaction surface temperatures in excess of 4000°K are easily achieved. Thus, we assume that in many (although not all) cases, we have observed vaporization taking place at or near critical conditions. Obviously, the conditions attained in laser-induced vaporization differ significantly from those in Langmuir or Knudsen vaporization experiments. Many species present in the vapor generated at extreme temperatures and pressures, conditions previously not achievable experimentally, are indeed different from those observed in the normal kind of vaporization experiments.

PROCEDURE

The laser-mass spectrometer consists of a TRG 104A Laser System coupled with a Bendix Time-of-Flight mass spectrometer. Ruby or Nd³⁺-doped glass laser rods emit pulses approximately 800 μsec in duration with maximum energies of about 5 joules. Details of the system have been reported elsewhere^{9,10}.

Since many of the laser-produced species vaporized as ions, we were able to record ionic as well as neutral mass spectra. Neutral spectra were obtained using 15 eV ionizing electrons; this was sufficient for ionization, but insufficient to cause much (undesirable) fragmentation. Spectra were usually recorded 500–600 μsec after the activation of the laser.

RESULTS AND DISCUSSION

In Table 1 the results of our studies of numerous substances are presented.

TABLE 1

COMPARISONS BETWEEN LASER-PRODUCED VAPOR SPECIES AND SPECIES OBSERVED IN CONVENTIONAL VAPORIZATION EXPERIMENTS

<i>Material</i>		<i>Laser vaporization</i>			<i>Conventional vaporization</i>	
<i>Substance</i>	<i>Species</i>	<i>Rel. abd. (ionic)</i>	<i>Rel. abd. (neutral)</i>	<i>Ref.</i>	<i>Rel. abd. (neutral)</i>	<i>Ref.</i>
Se	Se		20	12		28
	Se ₂	10	100			
	Se ₃	15	20		1.9	
	Se ₄	10	15		(5)	
	Se ₅	100	40		36.5	
	Se ₆	20	25		100	
	Se ₇	35	35		37.9	
	Se ₈	40	15		7.5	
	Se ₉	10				
Te	Te		10	15	11.	29
	Te ₂	10	65		100	
	Te ₃	15	10			
	Te ₄	5	5			
	Te ₅	100	100			
	Te ₆	10	10			
	Te ₇	15	15			
	Te ₈	1	1			
As	As		2	14	11	30
	As ₂		30		17	
	As ₃	15	20		8	
	As ₄	100	100		100	
	As ₅	30	5			
	As ₇	10	2			
Sb	Sb		1	15	9	28
	Sb ₂		10		15	
	Sb ₃	100	100		10	
	Sb ₄	90	80		100	
	Sb ₅	60	50			
Bi	Bi		100	13	60	31
	Bi ₂		90		100	
	Bi ₃	100	25		0.2	
	Bi ₄	30	5		2	
As ₂ O ₃ arseno- lite	As ₂		10	17		32
	As ₃		15			
	As ₄ O ₃	90	60			
	As ₄ O ₄	30	30			
	As ₄ O ₆	25	20		100	
	As ₅ O ₃	5				
	As ₅ O ₄	30	40			
	As ₅ O ₅	70	60			
	As ₅ O ₆	30	20			
	As ₆ O ₅	5	10			

TABLE 1 (continued)

<i>Material</i>		<i>Laser vaporization</i>			<i>Conventional vaporization</i>	
<i>Substance</i>	<i>Species</i>	<i>Rel. abd. (ionic)</i>	<i>Rel. abd. (neutral)</i>	<i>Ref.</i>	<i>Rel. abd. (neutral)</i>	<i>Ref.</i>
As ₂ O ₃ claude- tite	As ₆ O ₆	25	35			
	As ₇ O ₇	35	30			
	As ₈ O ₈	100	100			
	As ₉ O ₉	20	20			
	As ₁₀ O ₁₁	35	25			
	AsO	20	20	17		33
	As ₂ O ₂	70	40			
	As ₂ O ₃				25	
	As ₂ O ₄		30			
	As ₃ O ₃	40				
	As ₃ O ₄	70	50			
	As ₄ O ₂	25				
	As ₄ O ₃	25	65			
	As ₄ O ₄	100	100			
	As ₄ O ₆		35		75	
	As ₅ O ₃	30				
	As ₅ O ₄	70	55			
	As ₅ O ₅	10	55			
	As ₅ O ₆	40	20			
	As ₅ O ₇	40	25			
	As ₆ O ₆	10	15			
	As ₆ O ₇	35	45			
	As ₇ O ₆		20			
	As ₈ O ₁₀	40	40			
Sb ₂ O ₃ senarmon- tite	SbO	10	15	17		
	Sb ₂ O ₂	5	10			
	Sb ₃ O	2	5			
	Sb ₃ O ₄	100	100			
	Sb ₄ O ₅	10	15			
	Sb ₄ O ₆		10			
	Sb ₅ O ₇	75	75			
Sb ₂ O ₃ valente- nite	SbO	10	15	17		
	SbO ₅		2			
	Sb ₂ O ₂	15	10			
	Sb ₂ O ₄		5			
	Sb ₃ O ₄	100	100			
	Sb ₄ O ₅	15	15			
Bi ₂ O ₃	Sb ₅ O ₇	75	75			
	Bi	100	100	16		
	BiO	0	35			
	BiO ₃	20	20			
	Bi ₂	20	60			
	Bi ₂ O	15	25			
	Bi ₂ O ₂	15	25			
	Bi ₃	15	15			

TABLE 1 (continued)

<i>Material</i>		<i>Laser vaporization</i>			<i>Conventional vaporization</i>	
<i>Substance</i>	<i>Species</i>	<i>Rel. abd. (ionic)</i>	<i>Rel. abd. (neutral)</i>	<i>Ref.</i>	<i>Rel. abd. (neutral)</i>	<i>Ref.</i>
As ₂ S ₃	Bi ₃ O ₄	95	95			
	Bi ₄ O ₅	15	15			
	Bi ₄ O ₆	0	5			
	Bi ₅ O ₇	80	85			
	S ₂		60	17		
	AsS		10			
	As ₂		5			
	As ₃		5			
	As ₃ S	90	90			
	As ₃ S ₂	15	15			
Sb ₂ S ₃	As ₃ S ₃	20	20			
	As ₃ S ₄	100	100			
	S ₂		90	17		
	SbS		25			
	SbS ₅	10	10			
	Sb ₂ S ₃		5			
	Sb ₃ S	100	100			
	Sb ₃ S ₂	15	15			
Bi ₂ S ₃	Sb ₃ S ₃	25	25			
	Sb ₃ S ₄	25	25			
	S		40	16		34
	S ₂	5	100		100	
	Bi	25	20		II.	
	BiS		10		III.	
	Bi ₂	15	10		IV.	
	Bi ₂ S				V.	
	Bi ₂ S ₂				VI.	
	Pi ₃	95	60			
	Bi ₃ S	100	65			
	Bi ₃ S ₂	5	3			
	Bi ₃ S ₃	5	3			
	Bi ₃ S ₄	2	2			
	Bi ₄	20	20			
	Bi ₄ S ₆	35	30			
As ₂ Se ₃	Se	50	45	17		
	AsSe		10			
	As ₂		15			
	Se ₃	20	25			
	As ₄		5			
	As ₃ Se	100	100			
Sb ₂ Se ₃	As ₃ Se ₄	40	40			
	Se ₂		90	17		35
	SbSe		30		IV.	
	Sb ₂				III.	
	Sb ₂ Se ₂				II.	

TABLE 1 (continued)

<i>Material</i>		<i>Laser vaporization</i>			<i>Conventional vaporization</i>	
<i>Substance</i>	<i>Species</i>	<i>Rel. abd. (ionic)</i>	<i>Rel. abd. (neutral)</i>	<i>Ref.</i>	<i>Rel. abd. (neutral)</i>	<i>Ref.</i>
Bi_2Se_3	Sb_2Se_3		10			
	Sb_4				100	
	Sb_3Se	100	100			
	Sb_3Se_2	5	10			
	Sb_3Se_3	10	15			
	Sb_3Se_4	10	15			
	Se		25	16		35
	Se_2		100		II.	
	Bi	5	15		100	
	BiSe		30		III.	
	Bi_2	4	5		IV.	
	Bi_2Se	5	10			
	Bi_3	4	5			
	Bi_3Se	100	80			
	Bi_3Se_2	8	5			
As_2Te_3	Bi_3Se_3	10	10			
	Bi_3Se_4	8	5			
	Te		10	17		
	Te_2		20			
	As_2		15			
	As_3		10			
	As_4		20			
Sb_2Te_3	As_3Te	100	100			
	Te		25	17		35
	Te_2		100			
	Sb_2				III.	
	SbTe				IV.	
	Sb_4				100	
	Sb_2Te_2				II.	
Bi_2Te_3	Sb_3Te	100	75			
	Te		15	16		35
	Te_2		50		II.	
	Bi	15	15		100	
	BiTe	5	15		III.	
	Bi_2	5	5		IV.	
	Bi_2Te	15	10			
	Bi_3	5	5			
$\text{Bi}_2\text{Se}_{1.5}\text{Te}_{1.5}$	Bi_3Te	100	100			
	Se		5	16		
	Te		15			
	Se_2		100			
	SeTe	30	95			
	Te_2		90			
	BiSe	5	30			
	BiTe	15	15			

TABLE 1 (continued)

<i>Material</i>		<i>Laser vaporization</i>			<i>Conventional vaporization</i>	
<i>Substance</i>	<i>Species</i>	<i>Rel. abd. (ionic)</i>	<i>Rel. abd. (neutral)</i>	<i>Ref.</i>	<i>Rel. abd. (neutral)</i>	<i>Ref.</i>
BiSbTe ₃	Bi ₂		2			
	Bi ₂ Se		2			
	Bi ₂ Te		5			
	Bi ₃		10			
	Bi ₃ Se		50			
	Bi ₃ Te		80			
	Te		5	16		
	Te	5	20			
	Sb ₂ Te		5			
	Sb ₃ Te	100	100			
	Sb ₂ BiTe	70	60			
	SbBi ₂ Te	35	20			
As ₂ S _{2.5} Se _{2.5}	Bi ₃ Te	20	5			
	S ₂		25	14		
	SeS	30	30			
	Se ₂	35	35			
	As ₃ S	60	30			
	As ₃ Se	100	90			
	As ₃ S ₄	15	15			
	As ₃ S ₃ Se	60	60			
	As ₃ S ₂ Se ₂	80	100			
	As ₃ SSe ₃	60	65			
BiSbSeTe ₂	As ₃ Se ₄	15	15			
	SeTe	5	10	17		
	Te ₂	15	25			
	Sb ₃ S	80	80			
	Sb ₂ BiSe	20	20			
	Sb ₂ BiTe	70	80			
	SbBi ₂ Se	5	5			
	SbBi ₂ Te	35	35			
	Bi ₃ Se	2	2			
GaSb	Bi ₃ Te	5	5			
	Sb ₃ Te	100	100			
	Ga	100	100			28
	Sb		30		20.6	
	Sb ₂		15		36.7	
InAs	Sb ₃				10.4	
	Sb ₄				100	
	As		5		16	28
	In	100	90		2.2	
	As ₂	35	90		100	
	As ₃		35		5.6	
	As ₄		100		50	

TABLE 1 (continued)

<i>Material</i>		<i>Laser vaporization</i>			<i>Conventional vaporization</i>	
<i>Substance</i>	<i>Species</i>	<i>Rel. abd. (ionic)</i>	<i>Rel. abd. (neutral)</i>	<i>Ref.</i>	<i>Rel. abd. (neutral)</i>	<i>Ref.</i>
InTe	In	100	100		II.	36
	Te		2		IV.	
	InTe				V.	
	Te ₂	5	35		III.	
	In ₂ Te	60	50		100	
	In ₂ Te ₂				VI.	
	In ₃ Te	60	60			
	In ₃ Te ₂	5	5			
GeTe	Ge	20	25			37
	Te		25			
	Ge ₂	5	5			
	GeTe	60	60		100	
	Te ₂	60	60		8.9	
	Ge ₂ Te	5	5			
	GeTe ₂	100	100		1.3	
	Ge ₂ Te ₂	10	20			
	GeTe ₃	20	30			
	Ge ₂ Te ₃	30	40			
	GeTe ₄	2	5			
	Ge ₂ Te ₄	5	10			
	Ge ₃ Te ₄	10	15			
	Ge ₄ Te ₄	20	5			

The relative abundances of various peaks are listed, the most abundant peak in each spectrum being assigned a value of 100. Where available, the spectra resulting from conventional vaporization experiments are also presented for comparative purposes. In the case where the exact values of relative abundances are not known, only the order of abundance is specified by the appropriate Roman numeral.

The results listed in Table 1 indicate that in most cases there are significant differences between laser and conventional vaporization. These differences manifest themselves in (a) type of species; (b) relative abundance of species; (c) size of species, and (d) number of species present.

Species of the type A_3X_n , where $A = \text{As, Sb or Bi}$, $X = \text{S, Se or Te}$, and $n = 1, 2, 3, 4$, dominate the vapor above various chalcogenide compounds. It has been shown that these species emanate directly from the condensed phase and are not a result of the reaction occurring in the vapor phase¹⁴. Also, it was shown that these species are characteristic for the laser-induced vaporization only. The A_3X^+ species probably have a tetrahedral configuration, similar to tetrahedral As_4 and Sb_4 molecules¹⁶.

The correlation between the type of vapor species and the structure of the

condensed phase was discussed in refs. 13, 14, 16, and 17. In ref. 17 it was demonstrated that the structural differences between the As_2O_3 polymorphs are reflected in the type of vapor species present. The large relative abundance of A_3X_n species, even in systems where the concentration of A is very low, indicates that the metallic atoms are not randomly distributed in chalcogenide melts or glasses, but form clusters containing three or more atoms^{13,14}.

The relative abundances of various species are surprising in many cases, *e.g.*, Te_5 , Sb_3 and Bi_3 are the most abundant ionic species in the vapors above their respective solids; in conventional vaporization experiments these species are either only minor constituents of the vapor or do not exist at all.

The large number of species present in the laser-produced vapor could be a consequence of the following:

(i) Fragmentation may be due to the high temperatures produced in the laser-solid interaction; this, however, cannot be a principal cause, since most laser-produced species are actually larger than the conventionally produced ones.

(ii) If the laser-induced vaporization indeed takes place in the vicinity of the critical point, one would expect both large species and a large number of species, since in the critical region the heats of vaporization for all species drop to zero; thus, species not observable otherwise because of their large heats of vaporization could vaporize under critical conditions.

Clusters containing over 20 atoms (*e.g.*, $\text{As}_{10}\text{O}_{11}$) have been observed in our experiments. Large species usually have high heats of vaporization, *e.g.*, in the case of polymers, ΔH_v of a dimer is usually 5/3 to 9/5 times ΔH_v of a monomer³⁸. From the Clausius-Clapeyron equation it follows that the partial pressures of species with higher heats of vaporization increase more rapidly with temperature than those of species with lower values of ΔH_v . Thus, at higher temperatures the vapor contains more large species, and near the critical point many polymeric species will be present. The high relative abundance of unusually large species in our experiments is another indication that the laser-induced vaporization takes place at or in the vicinity of the critical region. This is the basis of our assumption that laser-produced species reflect some structural features of the condensed phase. In the vicinity of the critical region the difference between the density of the melt and its vapor decrease, finally disappearing at the critical point itself. Since density basically reflects the arrangement of atoms, molecules or other structural units, similarity in melt and vapor density will mean similarity in the type and arrangement of the structural units. Thus, studies of the vapor created in the vicinity of the critical point could yield information on the structure of the condensed phase, primarily the short range order structural features.

CONCLUSIONS

(1) The critical values of temperature and pressure can be reached in laser-solid interactions. Thus, the laser-mass spectrometer opens new possibilities for studies of substances under the conditions of extreme temperatures and pressures.

(2) The type, relative abundance, size and number of species present in the laser-produced vapor differ significantly from those in conventionally-produced vapor.

(3) In several cases it has been possible to correlate the structure of the condensed phase with the vapor species. This can be utilized in studies of short range ordering of some amorphous materials.

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